Comment on "Sponge-templated preparation of high surface area graphene with ultrahigh capacitive deionization performance"

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Comment on "Sponge-Templated Preparation of High Surface Area Graphene with Ultrahigh Capacitive Deionization Performance" by Yang et al.

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Capacitive deionization (CDI) is an emerging water treatment technology based on capacitive electrochemistry using porous carbon electrodes.[1] For water of relatively low salt concentration, CDI is envisioned to remove salt more effectively than the state-of-the-art methods in desalination, reverse osmosis and distillation.[2] In addition, practical employment of CDI for sea water treatment has come closer to realization with the development of flow-electrode CDI [3]. First experimental studies of CDI date back to 1960[4] and the field has seen an exponential increase in publication statistics since ~2008 (**Figure 1A**). More important than mere publication numbers is that our understanding of the ion removal process via reversible ion electrosorption in porous electrodes has significantly progressed over the last years. To mention but a few examples are porous electrode transport theory,[5] application of the modified Donnan (mD) model for ion electrosorption double layer theory,[6] novel in-situ measurement techniques of ion transport between electrodes,[7] and detailed rationalization of the contribution of each pore size increment on desalination performance [8].

1

With the emergence of novel carbon materials such as graphene and carbon nanotubes, more and more scientists explore CDI as a suitable application of novel forms of carbon. Yet, while exploring new carbon materials for CDI applications is of key significance to progress the field, it remains necessary to evaluate new developments and performance values in perspective of previously reported data and trends. This correspondence was prompted by the recent paper "*Sponge-Templated Preparation of High Surface Area Graphene with Ultrahigh Capacitive Deionization Performance*" by Yang *et al.*[9] The authors present results of a study using an interesting material, namely templated graphene which align well with results of studies of graphene for CDI over the last years by various authors.[10, 11-13]. The rationale is obvious: graphene with its excellent electrical conductivity and high specific surface area might present itself as an attractive electrode material for CDI.

Yet, the use of appropriate qualifying terminology is important; for instance, Yang *et al.* use the word "high surface area" to address their graphene foams that have a specific surface area of ~300 $m^2 \cdot g^{-1}$. In the field of carbon research this value cannot be considered as particularly high. Activated carbons[14] and specialty carbons, such as carbide-derived carbons,[15] have surface areas that may exceed 3000 $m^2 \cdot g^{-1}$ (Ref. [16]) while even the theoretical surface area of graphene[17] is 2630 $m^2 \cdot g^{-1}$.[18] Templated graphenes may have a lower surface area, but still values in the range of 800 - 1000 $m^2 \cdot g^{-1}$ have been reported.[19]

Pore size distribution is another very important aspect of CDI materials. Yang et al. show that their material preferentially contains pores between 3.5 nm and 90 μm. This pore size distribution (PSD) is considered by the authors to be favorable due to the fact that "larger pores can accommodate thicker electric double layer[s], resulting [in a] larger specific capacitance". However, it has been reported for CDI that micropores (i.e., pores smaller than 2 nm), and especially pores of sizes around and below 1 nm, exhibit the highest salt sorption capacity,[8, 20] in line with similar results for EDL-capacitors.[21] Thus, materials that are solely

meso- and macroporous, unless they excel in total surface area, are based on what has been shown in the literature not to be the most favorable for CDI electrodes.

More concerning than describing 300 $m^2 \cdot g^{-1}$ as a high surface area for porous carbons, is that Yang et al. chose, already in the title, to refer to the measured electrosorption capacity as "ultrahigh". As seen in **Figure 1B**, reported values for the salt adsorption capacity in CDI by carbon electrodes have steadily increased over the last years. Currently, values around 14 $mg \cdot g^{-1}$ are possible[8, 22] for systems based on pure ion electroadsorption (classic CDI) at the reference condition of a cell voltage of V_{cell}=1.2 V and in the optimal salt concentration range, which is around 5 - 50 mM.[23] Also recently, a salt adsorption capacity above 20 $mg \cdot g^{-1}$ for carbon materials modified with metal oxides has been reported.[11] Values for salt adsorption vary as a factor of applied cell voltage, initial salt concentration, setup design, and calculation method.[24] Thus, we provide an overview in **Table 1** of several different carbon materials and give information on selected operational parameters. We note that the value of 4.95 $mg \cdot g^{-1}$ reported by Yang et al. is actually rather small - especially when considering that a cell voltage of V_{cell}=1.5 V was used which was higher than the more commonly used cell voltage for laboratory testing of 1.2 V. Note that a performance of around 5 $mg \cdot g^{-1}$ had already been exceeded in 2008 as shown by work by Xu et al. (7.1 $mg \cdot g^{-1}$; Ref. [25]). Also, templated graphenes had been studied before, yielding a similar electrosorption capacity as reported in Ref. [9] (Ref. [12]: 3.9 $mg \cdot g^{-1}$). Thus, based on the data in **Figure 1B** and **Table 1**, we have to object to the statement "As far as we know, this is the highest value among the ever-reported carbon based electrode materials for CDI applications".

For commercial application of CDI, another aspect of CDI electrode performance is salt adsorption per period of time. This metric depends not only on the electrode architecture (mass density and macroporosity; Ref. [8]) but also on the system setup: electrode thickness, width of the flow channel, water flow rate, applied voltage, and cycle times (duration of salt adsorption and desorption step). Literature results show that in many experiments, close to

3

full saturation of CDI electrodes is easily achieved in a matter of a few minutes (e.g., Ref. [8, 26]). Thus, in our view, reference to a "significant desorption rate of 25 min" is unjustified, if it is implied that a desorption time of 25 min is shorter than previous work.

To report data of electrochemical testing, CDI, and carbon material analysis as effectively as possible, we make the following suggestions. First, it is useful to present geometrical information of the CDI cell, for instance on the electrode thickness, mass, and separation distance between the electrodes. Such information is of great help to the reader as it allows recalculation of derived numbers, such as salt adsorption capacity, from the experimental curve of desalination performance (e.g., Fig. 5 in Ref. [9]). This requirement of giving information on system dimensions is of particular relevance when only raw measurement data are presented, unscaled to electrode mass or volume, such as data given by Yang et al. for the "equivalent series resistance" (ESR) which are presented with unit Ohm. However, without knowing the dimensions of the test cell, such a number has no informative power, as it will scale with electrode dimensions.

A second suggestion is related to the fact that electrochemical testing in this work (CV, EIS) was performed in solutions with an ionic strength ranging from 0.5 - 1.5 M NaCl in water. Also results are reported for testing in 6 M KOH. However, in our view, such experimental data are less relevant for CDI, where the salinity of the water to be treated typically ranges between 10 - 100 mM. A relation with the actual experiments in this work is rather more tenuous as water was tested of 100 $\mu S \cdot cm^{-1}$ conductivity, which is about 1 mM NaCl. Porous carbon electrodes and desalination cells behave very differently when operated at 1 M NaCl compared to 1 mM NaCl, both with respect to the structure of the electrical double-layer (EDL), which determines ion storage, and with respect to ionic mass transport in the spacer channel and transport pathways within the electrode. Therefore, we urge for care in presenting in one work data of electrochemical testing in the range of 1 M together with desalination data obtained at 1 mM.

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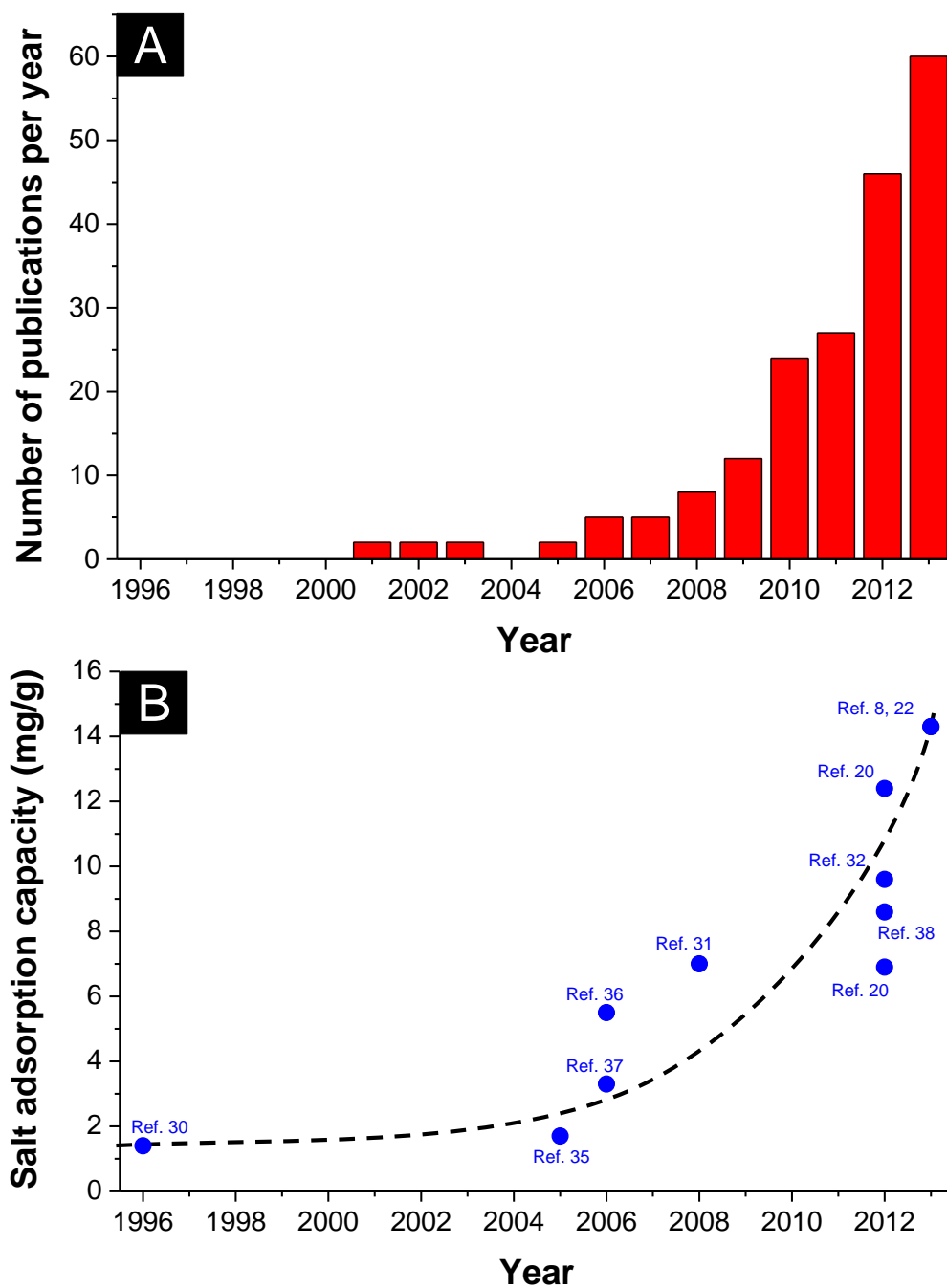
Figure 1. Number of publications per year for capacitive deionization (A) and development of NaCl electrosorption capacity reported for electrodes made of carbon materials (B; values and parameters are outlined in **Table 1**).

Table 1. Values for the salt adsorption capacity (mass of NaCl per total mass of both electrode combined) with selected measurement parameters. The values are clustered regarding the used material. All values are only for CDI without membranes and without metal oxide coatings.

Used material	Year	Salt adsorption (mg/g)	Cell voltage (V)	Initial salt concentration (mg/L)	Reference
Activated carbon	2010	3.7	1.5	200	[27]
	2010	10.9	1.2	290	[28]
		13.0	1.4	1170	[28]
	2011	10.5	1.2	1170	[29]
	2012	6.9	1.2	290	[20]
		6.1	1.2	25	[20]
	2013	14.3	1.2	290, 580	[8, 22]
Carbide-derived carbon	2012	12.4	1.2	290	[20]
		14.9	1.4	290	[20]
	2013	10.1 - 12.8	1.2	290	[8]
Carbon aerogel	1996	1.4	1.2	50	[30]
		2.9	1.2	500	[30]
	2008	7.0	1.3	2000	[31]
	2012	9.6	1.5	2900	[32]
Ordered mesoporous carbon	2008	0.68	1.2	25	[33]
	2009	0.93	0.8	50	[34]
Single-walled carbon nanotubes	2011	0.75	2.0	23	[13]
Multi-walled carbon nanotubes	2005	1.7	1.2	3000	[35]
	2006	5.5	1.2	5000	[36]
Multi-walled carbon nanotubes / nanofibers	2006	3.3	1.2	110	[37]
Graphene	2012	8.6	2.0	250	[38]